

Thermodynamics and kinetics of cashmere dyeing with metal complex dye

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The optimal condition, kinetics and thermodynamics of adsorption of the metal complex dye onto cashmere fibre have been studied in order to evaluate the improvement of cashmere qualities under industrial dyeing conditions with metal complex dye. The optimal conditions for dyeing cashmere fibre are obtained at 85°C temperature, 2-13% initial dye concentration, 3.5 pH and 50 min treatment time. By reducing the temperature and operating time, qualities of cashmere fibre such as luxury and softness improve, and damage to fibres decreases significantly. As a consequence, opportunities for enhancement of cashmere product quality and industrial efficiency due to mild industrial conditions and lower energy needs are attained. The adsorption kinetics of metal complex dye onto cashmere fibre follow a pseudo-second-order kinetic model with an activation energy of 77.33 kJ·mol⁻¹. The Langmuir isotherm is found the best model for dyeing adsorption onto cashmere fibre. On the basis of thermodynamics, kinetics and diffusion models, both adsorption and diffusion are involved in the process of dyeing cashmere, and an electrostatic attraction between dyeing molecules and cashmere fibre occurs.

Keywords: Adsorption, Cashmere fibre, C. I. Acid Red 315, Diffusion, Langmuir isotherm, Metal complex dye

1 Introduction

The cashmere of goats is one of the softest, warmest, and longest lasting materials in market, because the filament fibre of cashmere can hold air, keep warm, and is especially suitable for harsh, dry and mountainous climates. The most important intention of wool and cashmere industries is to manufacture textile products which satisfy consumers' needs. The dyeing process is the most crucial stage among the industrial stages for cashmere production from raw materials, such as sorting, washing, bleaching, dyeing, drying, blending, and spinning. However, the process of dyeing of cashmere fibre has not been examined sufficiently, and only a little technological research has been done, such as dyeing cashmere with reactive dye¹ and the process of dyeing cashmere at low temperatures². Meanwhile, the process of dyeing protein structured wool fibre whose morphological structure is similar to the cashmere fibre has been studied since the beginning of the 20th century. Methods for dyeing wool with chrome dyes have been studied³; furthermore, the interactions between wool and dyes⁴⁻⁷ have been examined. In recent years, the researchers have been focusing on application of the natural dyes, which are

eco-friendly, biodegradable and low toxic in the process of wool dyeing. They have studied the possibility of dyeing wool with the help of natural dyes extracted from *Chinese gall*⁸, *Hibiscus mutabilis*⁹, *Acacia cyanophylla*¹⁰, *Opuntia ficus-indica*¹¹ as well as *Indigo carmine*¹². The effect of factors, such as initial dye concentration, dye bath pH, temperature, concentration and types of a mordant has also been considered. Moreover, the dyes extracted from *Rheum emodi*¹³, *Bixa orellana*¹⁴, *Allium cepa*¹⁵, and *Punica granatum*¹⁶ have been used in wool dyeing process under the optimal conditions with regard to kinetic and thermodynamic parameters. There are some cases of using wool dyeing conditions in the cashmere dyeing industry¹⁷.

However, the cashmere cuticle which consists of outer cells of protein fibres has lower scale height compared to wool fibre; thus, it provides the soft handle, lustrous surface, lower shrinkage, and slippery nature¹⁸. A typical industrial condition for the dyeing process is an initial dye concentration of 2-5% depending on the color intensity of the products, a pH of 4.0-4.5 and a temperature of 96-98°C. Due to the high temperature (96-98°C) during the dyeing process, the softness and mechanical properties such as strength or tenacity and elongation of cashmere fibre significantly decrease, because the cuticles layer structure of the cashmere is damaged seriously.

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Accordingly, it is important to study the suitable operating procedures involved in dyeing of cashmere, considering the process mechanism. Many researchers have studied the mechanism of dyeing natural fibres with acid and reactive dyes which are mainly used for protein fibres. Kinetic, equilibrium isotherm and influencing parameters have been studied regarding the adsorption of reactive dyes onto cotton fibre¹⁹ along with the lac dyeing on cotton pretreated with chitosan²⁰. Chrastil²¹ studied adsorption kinetics of direct dyes on cotton and determined diffusion coefficients correlated with the chemical structures of direct dyes. The mechanism of dyeing cotton fabrics with a Procion blue dichlorotriazinyl reactive dye has been considered. Moreover, the simultaneous hydrolysis of the dye molecules with the physical binding and the chemical fixation, which is controlled by a solid-liquid interfacial process at the active sites onto the fabric, has been derived²².

Even though physico-chemical studies of the process of dyeing with the help of natural fibres such as cotton, silk and wool have been conducted, the mechanism of dyeing with the help of cashmere has not been examined sufficiently. On the other hand, it is necessary to improve the operating conditions for the dyeing process, which is an important stage in the manufacturing of the cashmere product. The present study is therefore undertaken to evaluate the optimal conditions for dyeing cashmere fibre with metal complex dye and to estimate the equilibrium isotherm, kinetic and thermodynamic parameters.

2 Materials and Methods

2.1 Materials

Light colored, 2nd grade natural cashmere fibre with a diameter of 16.7 μm was used after pretreatment in a primary factory, Tuya Co. Ltd. C. I. Acid Red 315 dye (Hebei Zhongzhou Import and Export Trade Co. Ltd.) was selected as a metal complex dye for the dyeing process. The chemical formula of C. I. Acid Red 315 dye is disodium/2,4-dihydro-4-/(2-hydroxy-4-nitrophenyl) azo/-5-methyl-2-phenyl-3H-pyrazol-3-onato(2-)/3-yl azo/-2-hydroxy-5-nitrobenzenesulfonato (3-)/chromate (2-). Sodium sulfate was chosen as a levelling agent. All other chemicals used in this study were of LR grade.

2.2 Dyeing Procedure

The dyeing was carried out in a batch system. During each experiment, 1.000 g of cashmere was

added to 200 mL of the dye solution in a 250 mL beaker with a constant ratio of levelling agent to dye. Solution media was adjusted with pH/mV/°C bench meters (Hanna HI 2211) with 1 M acetate (pH 3.50-5.50) and 1 M phosphate (pH 6.50-8.50) buffer solutions. As the commercial dyes are used for dyeing cashmere under industrial conditions, the amount of the levelling agent was kept the same, and the effect of amount and types of the levelling agent was not considered. The optimal condition was fixed as: initial dye concentration 0.5 – 22.0% [(weight of dry dye in g/weight of fibre in g)×100%], pH 3.50 – 8.50, temperature 60.0 – 95.0°C and treatment time 50 min. The cashmere samples were cooled down to room temperature, washed with distilled water and then dried at ambient temperature. The remaining concentration in the dye solution with contact time was analyzed with spectrophotometric method (UV/VIS Cary 60) at 490 nm of wavelength. The dye uptake [q_t (mg·g⁻¹)] was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad \dots (1)$$

where C_0 and C_t are the dye concentration (mg·L⁻¹) initially and at a given time t respectively; V , the volume of dye solution (L); and W , the weight of cashmere fibre (g).

The study of adsorption kinetics was done in the batch system. 200 mL dye solution (2.0%) and 1.000 g of cashmere fibre were added in a 250 mL beaker and mixed for 50 min at various temperatures, such as 70°C, 75°C, 80°C, 85°C, 90°C and 95°C. The pH of all experiments was adjusted at 3.50 using 1M acetate buffer solution. The remaining dye concentration in the dye solution with contact time was analyzed with a spectrophotometric method.

2.3 Characterization of Cashmere Fibre

Mechanical properties such as strength or breaking tenacity and fibre elongation of natural and dyed cashmere fibres were measured according to the MNS5821:2007 standard using a stelometer (USTER Stelometer 754, Italy) and the process was repeated 10 times (MNS 5821:2007). The condition of analysis was 20°C ± 2°C temperature and 60 ± 5% humidity. The cashmere fibre sample was kept in a desiccator for 12-24 h under standard conditions to prepare the measurement.

3 Results and Discussion

3.1 Determination of Optimal Condition

3.1.1 Effect of Initial Dye Concentration

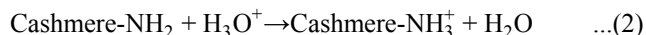
Effect of initial dye concentration on cashmere dyeing was investigated by altering the initial concentration from 0.5% to 22.0% for 50 min, keeping the other parameter constant as 4.50 pH, 1.000 g cashmere fibre, and 95.0°C temperature. The dependence of the dye uptake on the initial dye concentration is shown in Fig. 1.

The dye uptake increases from 4.64 mg·g⁻¹ to 84.8 mg·g⁻¹ when the initial dye concentration is increased from 0.5% to 13.0%, and after that the dye uptake decreases dramatically to 68.8 mg·g⁻¹ with the increase in initial concentration to 22.0 %. This may be due to a nearly complete coverage of the binding sites of cashmere. In addition, on increasing initial dye concentration, the number of collisions between dye anions and cashmere fibre increases, followed by enhancement of the dyeing process²³. Beyond 13.0% initial dye concentration, the dye uptake decreases, because dye uptake of the process depends on binding sites of the cashmere. On the other hand, this principle indicates that a monolayer of dye molecules is formed over the cashmere surface and the process couldn't take place. A dye solution with a dye concentration of 13.0% can be adsorbed on cashmere binding sites due to the formation of monolayer. Hence, 0.5-13.0% dye concentration of dye solution is selected as an optimum concentration. However, 2.0-5.0% dye concentration is used under industrial conditions; 2.0% is chosen in further experiments.

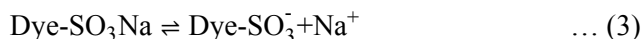
3.1.2 Effect of Initial pH

The pH of the dye solution is one of the important parameters for the dyeing process. The effect of initial pH on the dyeing process has been investigated in the pH range 3.10 – 8.50 at 90.0°C with 2.0% of the initial dye concentration for 50 min (Fig. 2).

Figure 2 shows that the dye uptake increases from 18.66 mg·g⁻¹ to 18.95 mg·g⁻¹ with an increase in pH from 3.10 to 3.50, whilst the dye uptake decreases from 18.95 mg·g⁻¹ to 13.40 mg·g⁻¹ with an increase in pH from 3.50 to 8.50. The effect of dye solution pH can be attributed to the correlation between the molecular structures of dye and the fibre. Cashmere (isoelectric point ~ 4.60) will have a net positive charge due to the protonation of nitrogen-containing functional groups such as amines at an acidic pH^{10, 24}, as shown below:



C. I. Acid Red 315 is a metal complex dye, dissociated by sulfonyl anion under acidic (pH 3.5) conditions, as can be seen below:



Sulfonyl groups would interact with the protonated amino groups of cashmere fibres under acidic conditions, as shown below:



The pH increases with the decrease in number of hydronium ions and hence increases the number of

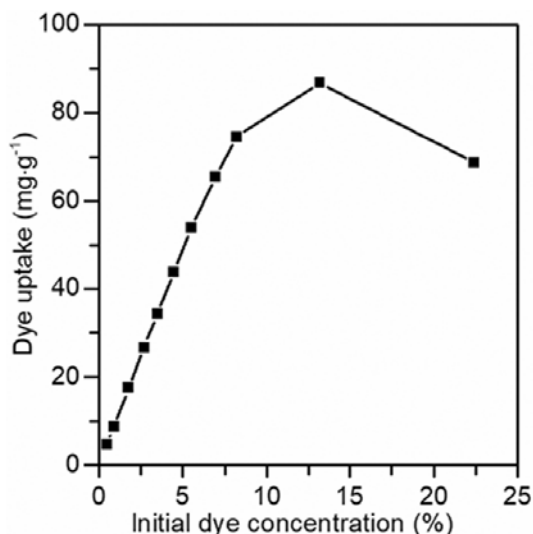


Fig.1 — Relation between dye uptake and initial dye concentration (pH 4.50, *t* 95°C, *t'* 50 min)

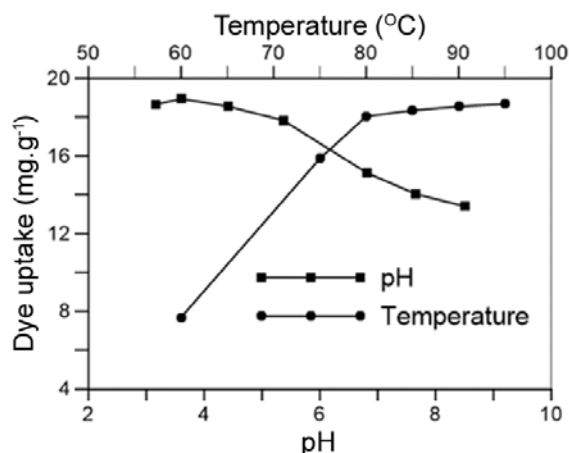


Fig.2 — Effect of pH and temperature on dyeing process (*C*₀ 2.0%, *t* 90.0°C, pH 4.50, *t'* 50 min)

hydroxyl ions. Therefore, as the number of protonated amino groups of fibres decreases, the intermolecular interaction also decreases. Since the dye used in this study carries some negative charge due to sulfonyl groups (Fig. 1), electrostatic attractions are expected to make a considerable contribution to the overall interactions. Furthermore, dispersive interactions and hydrogen bonding should still be operative between dye species and cashmere fibre simultaneously²⁵. Hence, the dye uptake decreases from $18.95 \text{ mg}\cdot\text{g}^{-1}$ to $13.40 \text{ mg}\cdot\text{g}^{-1}$ while the initial pH of solution increases from 3.5 to 8.5. Even if the highest dye uptake is achieved at pH 3.50, it is found that from pH 3.50 to 4.50, the dye uptake slightly decreases from $18.95 \text{ mg}\cdot\text{g}^{-1}$ to $18.55 \text{ mg}\cdot\text{g}^{-1}$, which could be considered almost constant. Some researchers reported similar results, i.e. dyes are effectively adsorbed on wool consisting of protein fibre (like cashmere) under acidic conditions^{13, 24}. In addition, too low pH value is not suitable for industrial processes because it results in a rapid dye uptake, limited migration, and poor levelness. Therefore, the optimum pH of the initial dye solution for the experiments is fixed at 4.50 which is just below the isoelectric point of the cashmere.

3.1.3 Effect of Temperature

The effect of temperature on the dyeing process is studied, considering temperature range 60.0°C - 95.0°C , pH 4.50, an initial dye concentration 2.0% and treatment time 50 min. The results obtained are presented in Fig. 2.

The dyeing rate decreases gradually for the first 50 min at all temperatures. The dyeing process could not achieve an equilibrium at temperatures in the range of 60°C - 80°C . Moreover, the dye uptake is less than that measured at a temperature range 85°C - 95°C . At 85°C - 95°C temperature range, the dyeing process attains an equilibrium at the maximum adsorption capacity of $18.50 \text{ mg}\cdot\text{g}^{-1}$ within 30 min and the process rates are found almost the same at all temperatures (data not shown here). As a relation between adsorption capacity and temperature (Fig. 2), the dye uptake is increased 2.4 times from $7.68 \text{ mg}\cdot\text{g}^{-1}$ to $18.04 \text{ mg}\cdot\text{g}^{-1}$ with the increase in temperature from 60°C to 80°C . The dye uptake becomes relatively stable beyond a temperature of 80°C . The applicable operating time and temperature selected are 50 min and 80°C respectively.

The surface of the cuticle cells of cashmere is highly hydrophobic due to covalently bound fatty

acids and the high amount of disulfide bridges²⁶. Thus, dye molecules are poorly adsorbed onto cashmere fibre from aqueous media because of the cashmere's higher hydrophobicity at relatively lower temperature. Similar patterns in the graph of dye uptake vs operating time have been observed, and the maximum dye uptake is found to be almost the same at temperatures higher than 85°C . It can be explained by the following reasons: (i) at higher temperature, the dye uptake increases with rising cashmere wettability, and (ii) the intraparticle diffusion rate of adsorbate is enhanced with rising temperature because the random motion of the dye molecules and, consequently, their kinetic energy are increased²³. Increasing of dye uptake with temperature indicates that spontaneity of process increases and endothermic process occurs²⁷. Hence, 85.0°C is selected as the optimal temperature for further experiments.

In order to investigate the possibility for technological development, the tenacity and elongation of cashmere fibres after dyeing under optimal conditions are compared with those of natural and dyed cashmere fibre under industrial conditions (Fig. 3). The tenacity and elongation of dyed cashmere fibre under optimal conditions are measured as $9.77 \text{ g}\cdot\text{tex}^{-1}$ and 3.03% respectively.

The tenacity and elongation of dyed cashmere fibre under optimal conditions are lower than those of natural cashmere fibre and higher than those of dyed cashmere fibre under industrial conditions. This result indicates that there is a potential of saving energy of industry as well as improving the productivity and quality of cashmere fibre, thereby retaining its luxury and softness as well as lowering the damage to fibres by upgrading industrial conditions such as operating

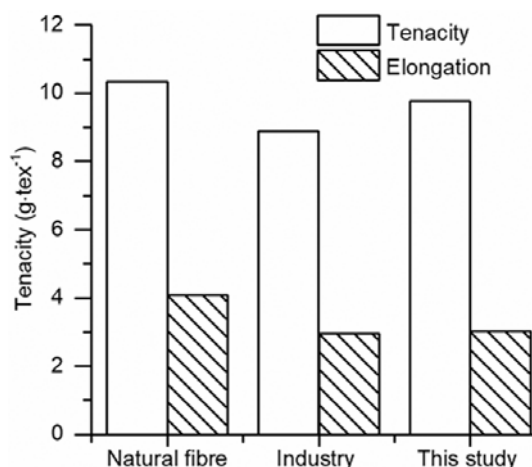


Fig.3 — Comparison of cashmere quality parameters

time, temperature and pH. In particular, it is possible to optimize industrial conditions (t 85°C, pH 3.5, C_0 2%), as examined in this study.

3.2 Adsorption Isotherm

The subsequent processes of adsorption and diffusion are considered as a rate determining step of the processes of dyeing cashmere fibre. In the present study, the experimental data of the adsorption equilibrium between the amounts of adsorbed and remaining dye in a solution under optimal conditions are used to describe appropriate isotherm models such as the Langmuir and Freundlich models^{28, 29}.

To describe the applicability of the Freundlich and Langmuir isotherm models, a linear plot of $\ln q_e$ versus $\ln C_e$ and C_e/q_e versus C_e is plotted and the calculated parameters are summarized in Table 1. Langmuir isotherm model is found to be the best model for dye adsorption onto cashmere fibre at a selected temperature range. According to the Langmuir theory, there are few adsorption sites on cashmere fibre and only one dye molecule can be adsorbed on each of these sites of cashmere fibre. Hence, adsorbed dye molecule cannot be moved freely on the surface. Adsorption occurs through formation of a monolayer of dye molecules on the cashmere fibre.

The value of R_L is found in the range of 0.023-0.011, which indicates that adsorption of dye on cashmere fibre is favorable³⁰. Regarding the Langmuir model, a monolayer of dye is formed over a uniform cashmere fibre with relatively strong electrostatic interaction.

On increasing temperature from 75°C to 85°C, Langmuir constant and maximum adsorption capacity increase from 0.45 L·mg⁻¹, 54.64 mg·g⁻¹ to 0.77 L·mg⁻¹, 77.52 mg·g⁻¹ respectively. The higher the q_{\max} and K_L are, the higher is the affinity of dye for the cashmere fibre. As the temperature increases, the equilibrium shifts forward or towards the adsorption side, and therefore K_L increases. We can conclude that the adsorption will occur favorably at higher temperatures. However, at 90°C the Langmuir

constant decreases steeply to 0.18 L·mg⁻¹, because the diffusion, which occurs simultaneously with the adsorption, is promoted at high temperature.

Moreover, the thermodynamic functions [activation Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)] for adsorption of dye onto cashmere fibre are considered. The positive value of enthalpy (55.68 kJ·mol⁻¹) indicates that the adsorption of dye onto cashmere fibre is endothermic, showing that adsorption capacity is directly proportional to temperature. Typical values of enthalpy of adsorption are in the region of 20 kJ·mol⁻¹ for the physisorption and in the region of 200 kJ·mol⁻¹ for the chemisorption³¹. The relatively high value of enthalpy seems reasonable because of the associative chemisorption between dye and cashmere fibre. When the adsorption is endothermic, the increase of adsorption entropy is the principal factor for the spontaneity of adsorption. If the temperature is raised, $\Delta H^\circ/T$ is smaller and as a result, the equilibrium shifts towards the right side³¹. The positive value of entropy (153.5 J·mol⁻¹·K⁻¹) indicates that as the temperature increases, the temperature randomness of the molecules during the adsorption and the distribution of energy increase. The value of ΔG° for adsorption decreases from 2.27 kJ·mol⁻¹ to 0.73 kJ·mol⁻¹ with an increasing temperature from 75°C to 85°C. It means adsorption is favorable at relatively high temperatures.

3.3 Adsorption Kinetics

Adsorption rate is proportional to the amount of adsorbed materials. Adsorption kinetic models are applied to interpret the experimental data and to control adsorption mechanism.

In the present study, kinetic data is analyzed using pseudo-first order and pseudo-second order models (on the basis of linearity) which are most frequently used for describing adsorption systems.

Adsorption rate constants and equilibrium adsorption capacities are estimated in Table 2. The data obtained for the graph fitted with good

Table 1 — Isotherm parameters of adsorption of dye onto cashmere fibre

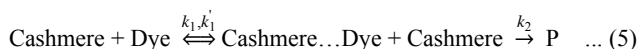
| Temp. (t), °C | Langmuir isotherm | | | | Freundlich isotherm | | |
|----------------------|---------------------------------|----------------------------|-------|--------|----------------------------|-----|--------|
| | q_{\max} , mg·g ⁻¹ | K_L , L·mg ⁻¹ | R_L | R^2 | K_F , L·mg ⁻¹ | n | R^2 |
| 75 | 54.64 | 0.45 | 0.023 | 0.9986 | 20.03 | 3.9 | 0.8028 |
| 80 | 62.11 | 0.62 | 0.017 | 0.9980 | 24.75 | 4.1 | 0.6188 |
| 85 | 77.52 | 0.77 | 0.011 | 0.9998 | 35.24 | 4.8 | 0.4859 |
| 90 | 126.58 | 0.18 | 0.061 | 0.9998 | 31.78 | 3.4 | 0.7485 |

Table 2 — Adsorption and diffusion rate constants with different models

| Temp. (<i>t</i>), °C | Pseudo I order model | | Pseudo II order model | | | Intramolecular diffusion model |
|---------------------------|---------------------------|----------------|----------------------------|--|----------------|---|
| | k_1 , min ⁻¹ | R ² | q_e , mg·g ⁻¹ | $k_2 \times 10^{-3}$, g·mg ⁻¹ ·min ⁻¹ | R ² | k_D , mg·g ⁻¹ ·min ^{-1/2} |
| 70 | 0.042 | 0.9838 | 21.55 | 2.40 | 0.9958 | - |
| 75 | 0.092 | 0.9369 | 21.74 | 3.91 | 0.9963 | - |
| 80 | 0.120 | 0.9970 | 20.88 | 8.17 | 0.9977 | 1.53 |
| 85 | 0.128 | 0.9933 | 21.32 | 9.32 | 0.9964 | 2.19 |
| 90 | 0.167 | 0.9935 | 21.28 | 12.08 | 0.9965 | 3.02 |
| 95 | 0.214 | 0.9857 | 21.32 | 15.50 | 0.9986 | 2.25 |

correlation coefficients ($R^2=0.9958 - 0.9986$), indicate that the adsorption kinetics of dye onto cashmere fibre follow the pseudo II order model. The pseudo II order model is based on the assumption that the rate limiting step may be chemisorption, which involves valence forces by sharing or electron exchange between adsorbate and adsorbent³². The equilibrium adsorption capacities (q_e), calculated from the pseudo II order model, are found in accordance with the experimental values, which implies that the adsorption obeys a pseudo second order model. As the temperature increases from 75°C to 90°C, the adsorption rate constant increases from 2.40×10^{-3} g·mg⁻¹·min⁻¹ to 15.50×10^{-3} g·mg⁻¹·min⁻¹. The higher the temperature, the higher is the adsorption rate constant. Moreover, the adsorption will speed up at higher temperatures.

Following the pseudo II order model, the adsorption of dye onto cashmere fibre may occur through the following mechanism forming an activated complex in intermediate stage³³:



where cashmere...dye is activated complex formed in intermediate stage

The rate law for an activated complex can be written by using a steady state approximation as follows:

$$\frac{d[\text{Cashmere} \dots \text{Dye}]}{dt} = k_1[\text{Cashmere}][\text{Dye}] - k_2[\text{Cashmere} \dots \text{Dye}] - k_3[\text{Cashmere} \dots \text{Dye}][\text{Cashmere}] \approx 0 \quad \dots (6)$$

The steady state concentration of Cashmere...Dye will be

$$[\text{Cashmere} \dots \text{Dye}] = \frac{k_1[\text{Cashmere}][\text{Dye}]}{k_2 + k_3[\text{Cashmere}]} \quad \dots (7)$$

Accounting for the steady state concentration of intermediate, the total adsorption rate law can be written as follows:

$$\frac{d[P]}{dt} = \frac{k_3 k_1 [\text{Cashmere}]^2 [\text{Dye}]}{k_2 + k_3 [\text{Cashmere}]} = k_{\text{eff}} [\text{Cashmere}]^2 [\text{Dye}] \quad \dots (8)$$

For a steady state approximation, the concentration of intermediate must be almost constant. So k_1 does not have to be much bigger than k_2 and k_3 for the approach to be reasonably accurate³¹. For this reason, k_1 is the rate determining step which controls the overall rate of the process. It is assumed that if the adsorption capacity is proportional to the number of active sites occupied on the cashmere fibre and the concentration of dye is constant, then the kinetic rate law can be rewritten as pseudo II order kinetics. This is the evidence that the adsorption kinetics of dye onto cashmere fibre obey the pseudo II order model.

The activation energy and frequency factor are calculated as 77.33 kJ·mol⁻¹ and 3.14×10^9 respectively. The value of E_a indicates whether a physical or chemical adsorption process occurs³⁴. In physical adsorption, the interaction is easily reversible, equilibrium is rapidly attained and its energy requirements are small, so E_a is usually not more than 5-40 kJ·mol⁻¹, while in chemical adsorption much stronger bonding forces are involved and E_a values range 40-800 kJ·mol⁻¹. It follows that the adsorption of dye onto cashmere fibre most likely involves a chemisorption process consistent with electrostatic interaction.

3.4 Intraparticle Diffusion

The intraparticle diffusion model was used to calculate the diffusion rate constant of adsorption of dye onto cashmere fibre³⁵. The diffusion model is expressed as follows:

$$q_t = k_D \cdot t^{1/2} \quad \dots (9)$$

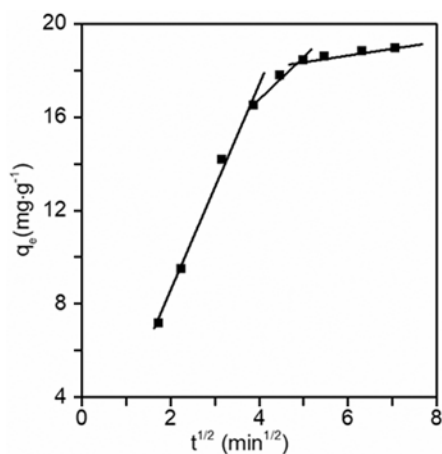


Fig. 4 — Kinetics of intramolecular diffusion at 85°C (C_0 2%, pH 3.50, t 85°C)

where q_t is the adsorption capacity at any time ($\text{mg}\cdot\text{g}^{-1}$); and k_D , the diffusion rate constant ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$).

Using Eq. (9), the diffusion rate constant can be calculated from the slope for the linear plot q_t versus $t^{1/2}$ (Fig. 4).

Multilinear dependence is observed indicating that three steps took place and the dyeing process of cashmere is a complex or multistep process. The first, steeper line is attributed to the adsorption of dye onto the surface of cashmere fibre³⁶. The second line describes the intraparticle diffusion which is the rate limiting step, indicating the gradual diffusion of dye molecules through adsorbed molecules onto cashmere fibre. The third line is attributed to the ultimate equilibrium step for which the intraparticle diffusion started to slow down due to the extremely low dye concentration left in the solution³⁷. Furthermore, diffusion cannot be the only rate determining step because no straight line passes through the origin of coordinates^{37, 38}. The calculated diffusion rate constant at different temperatures is presented in Table 2. As the temperature increases, the diffusion rate constant increases in the range of 80°-90°C, and then decreases at 95°C. As the active sites on the cashmere surface are completely occupied with dye molecules, the diffusion of dye molecules through the adsorbed molecules would be limited at high temperature. It can be concluded that adsorption is the rate determining step at relatively lower temperature even though the increasing temperature diffusion step tends to be the rate determining step.

4 Conclusion

Optimal conditions for the dyeing process of metal complex dye onto cashmere fibre are obtained as 85.0°C temperature, 2.0-13.0% initial dye concentration, 4.50 pH and 50 min treatment time. The measured values of cashmere fibre tenacity and elongation in the case of both new and conventional conditions are found to be similar, showing that the obtained condition can be applicable for industry. It is shown that the application of an industrial dyeing temperature and an operating time of 85°C and 50 min instead of 96°C -98°C and 80 min respectively is feasible. By reducing the temperature and operating time, benefits such as energy saving, less damage to fibres and improvement of cashmere fibre quality, such as keeping its luxury and softness, can be obtained.

Both adsorption and diffusion are likely to happen during the dyeing process. The kinetics of the adsorption are found to obey the pseudo-second-order model and it has been found that kinetically stable complex is formed. Moreover, the adsorption isotherm is found fitted to Langmuir isotherm model. On the other hand, it is found that metal complex dye forms a monolayer on the surface of cashmere fibre with chemical adsorption. Looking at the thermodynamics study, the value of ΔG° for adsorption decreases with increasing temperature, and adsorption is favored at high temperatures. This means that the adsorption of dye onto cashmere fibre is a thermodynamically unstable and unspontaneous process. The study of the intraparticle diffusion model reveals that the diffusion process may not be the only rate determining step. The chemical adsorption of dye molecules onto cashmere fibre occurs with electrostatic attraction forces between amine groups in cashmere fibre and sulfonyl groups in dye molecule on the basis of high activation energy and thermodynamic functions.

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